Title: Structural and magnetic properties of Fe3-xTixSn disordered alloys

Author: Krzysztof Brząkalik

Citation style: Brząkalik Krzysztof. (2008). Structural and magnetic properties of Fe3-xTixSn disordered alloys. "Acta Physica Polonica A" (Vol. 114, nr 6 (2008), s. 1529-1536).

Proceedings of the Polish Mössbauer Community Meeting 2008

Structural and Magnetic Properties of $Fe_{3-x}Ti_xSn$ Disordered Alloys

K. Brzakalik*

Institute of Materials Sciences, University of Silesia
Bankowa 12, 40-007 Katowice, Poland

A series of $Fe_{3-x}Ti_xSn$ disordered alloys (where $x = 0$, 0.25, 0.5, and 0.75) obtained by arc-melting were studied. Directly after the melting all samples were mechanically crashed and in that form examined by the X-ray diffraction and Mössbauer effect methods. In $Fe_{3-x}Ti_xSn$ alloy with $x = 0$ three phases exist: FeSn (B35), $FeSn_2$ (C16) and Fe(Sn) (A2). The contributions of these phases decrease very fast in aid of ternary Fe–Ti–Sn alloys with the $B2$ and $D0_3/L2_1$ types of structure, as Ti atoms concentration increases. It was shown that these ternary alloys consist of four distinct Fe–Ti–Sn phases with contributions depending on the value of the x parameter. The value of hyperfine magnetic field ($B_{\rm hf}$) parameter at the Fe nuclei is equal to about 110 kG for FeSn and $FeSn_2$ phases. However in alloys with $A2$, $B2$ and $D0_3/L2_1$ type of structure this value changes from 0 kG to 335 kG and can be considered (in the first approximation) as a function of Fe atoms number in the nearest neighborhood.

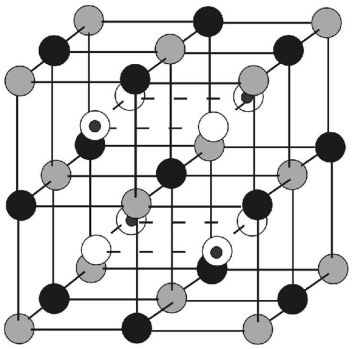
PACS numbers: 61.05.cp, 75.50.Bb, 76.80.+y

1. Introduction

The ternary $Fe_{3-x}Ti_xSn$ alloys belong to the class of iron-based alloys of the general composition $Fe_{3-x}Y_xZ$, where Y is a transition metal (Y = Mn, Cr, Ti, V, Co, Ni) and Z is a nonmagnetic element (Z = Al, Sn, Ga or Si). Most of them have the $D0_3$ crystal structure when $x = 0$, the $D0_3/L2_1$ structure when $0 > x > 1$ and the Heusler $L2_1$ structure when $x = 1$ [1–4]. The Fe_3Sn ordered alloy has the $D0_{19}$ crystal structure [5], however the Fe_2TiSn alloy crystallizes to the $L2_1$-type (Fig. 1) in which 8c site is entirely filled by Fe atoms, the 4a site includes only Ti atoms whereas 4b site is completely occupied by Sn atoms [6, 7]. This Heusler-type alloy belongs to the group of systems in which the local environment strongly influences the electronic and magnetic properties. It was shown in paper [7] that the value of the magnetic moment on iron changes from 0 to 2.7 $\mu_{\rm B}$. In paper [8]

*e-mail: kbrzakal@op.pl

transport properties of non-stoichiometric $Fe_{3-x}Ti_xSn$ ($x = 0.9$, 0.95, 1.0, 1.05 and 1.1) alloys were also investigated. It was shown that electrical resistivity in alloys with $x = 1$, 1.05 and 1.1 exhibits metallic behavior whereas the alloy with $x = 0.95$ exhibits semiconductor-like behavior above the Curie temperature of 120 K. These results suggest that the $Fe_{2.05}Ti_{0.95}Sn$ compound should be a semimetal with a pseudogap in the density of states at the Fermi level.



Sites →	4a	4b	8c
FeSn (B2)	Sn	Sn	Fe
$Fe_{3-x}Ti_xSn$ ($D0_3/L2_1$)	Sn	Fe Ti	Fe
Fe_2TiSn ($L2_1$)	Sn	Ti	Fe

Fig. 1. Crystal structure and site occupancy of $B2$, $D0_3/L2_1$ and $L2_1$ structure of $Fe_{3-x}Ti_xSn$ alloys.

In the earlier paper [9] some results of $Fe_{3-x}Ti_xSn$ ordered alloys were reported. The *ab initio* calculations of the electronic structure show that for Fe atoms from the 8c site, the calculated values of isomer shift (IS) and hyperfine magnetic field ($B_{\rm hf}$) parameters are linearly correlated. The value of $B_{\rm hf}$ changes linearly from 0 kG to 130 kG when the number of iron atoms from the nearest neighbor change from 0 to 4. The Fe atoms from 4a sites have a constant value of $B_{\rm hf}$ equal to 347 kG.

The goal of this paper is to provide an analysis of the structural and magnetic properties of $Fe_{3-x}Ti_xSn$ disordered alloys (where $x = 0$, 0.25, 0.5 and 0.75) obtained by arc-melting.

2. Experimental

The investigated $Fe_{3-x}Ti_xSn$ alloys (where $x = 0$, 0.25, 0.5, and 0.75) were prepared by arc-melting in the high purity argon gas atmosphere from materials of 99.99% purity. Directly after melting the samples were mechanically crashed and in that form examined by the structural and Mössbauer methods.

The X-ray measurements were made at room temperature on powder samples using a Philips PW 1130 diffractometer with Cu K_α radiation. These data were analyzed using a PCW program [10].

The ^{57}Fe Mössbauer spectra were recorded at room temperature using a conventional constant acceleration spectrometer with a ^{57}Co(Rh) source with an activity of about 50 mCi. Main analysis of the Mössbauer spectra was performed

with the use of a private software program, however the first steps were made taking advantage of the Hesse and Rübartsch methods [11].

3. Results and discussion

The X-ray patterns collected in Fig. 2 revealed that the $Fe_{3-x}Ti_xSn$ disordered alloy system exhibits multi-phase microstructures, consisting of the compounds such as FeSn (with $B35$ type of structure), $FeSn_2$ ($C16$), Fe(Sn) ($A2$) and ternary Fe–Ti–Sn phases with $B2$, $D0_3$ and $L2_1$ types of structure.

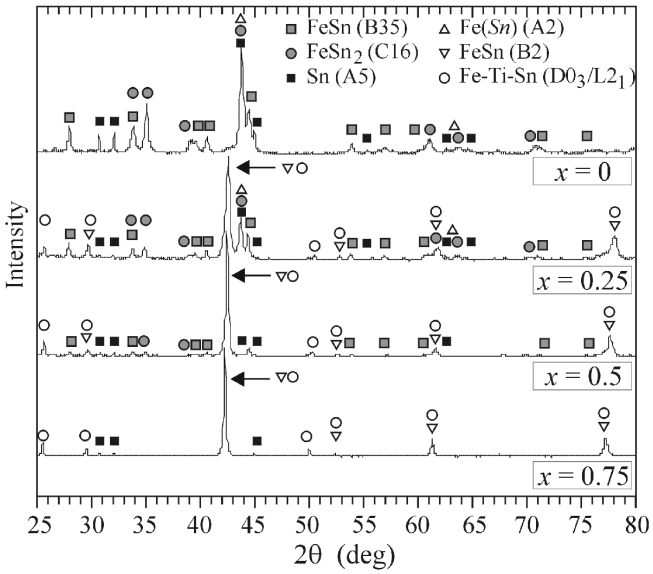


Fig. 2. X-ray patterns of $Fe_{3-x}Ti_xSn$ disordered alloys.

There was not observed any amount of Fe_3Sn alloy with $D0_{19}$ type of structure in $Fe_{3-x}Ti_xSn$ disordered alloys with $x = 0$, instead, there exist FeSn, $FeSn_2$ and Fe(Sn) phases with the contribution of 37.2%, 26.2%, and 25.5%, respectively (Table). The first two of them occur in alloys with Ti concentration $x \leq 0.5$. The lattice parameters of FeSn and Fe_2Sn phases which exist in system with $x = 0$ correspond to those reported in papers [5, 12, 13] and are somewhat larger in alloys with $x > 0$ which can be explained by partial substitution of Fe atoms by Ti atoms. The Fe(Sn) alloy with $A2$ crystal structure exists only up to Ti atoms concentration with the contribution of 22.2%. Its lattice parameter increases from 2.922 ± 0.001 Å (for $x = 0$) to 2.928 ± 0.001 Å (for $x = 0.25$), which by comparison with the data of the Fe–Sn system reported in paper [14] can suggest that the content of Sn atoms in Fe(Sn) phase changes from 8 at.% to 10 at.%.

The X-ray studies reveal that as early as x parameter equals to 0.25 the peaks associated with the Fe–Ti–Sn ordered phases with $B2$, and $D0_3/L2_1$ type

TABLE

The lattice parameters (a, c) and contributions (con) of phases existing in $Fe_{3-x}Ti_xSn$ disordered alloys.

Phase	Data from literature	This paper (error of the lattice parameters is equal to 0.001 Å)			
		$x = 0$	$x = 0.25$	$x = 0.5$	$x = 0.75$
FeSn ($B35$)	$a = 5.300$ Å $c = 4.449$ Å^{a}	$a = 5.297$ Å $c = 4.441$ Å con = 37.3%	$a = 5.304$ Å $c = 4.441$ Å con = 15.1%	$a = 5.304$Å $c = 4.443$ Å con = 7.9%	–
$FeSn_2$ ($C16$)	$a = 6.539$ Å $c = 5.325$ Å^{*,b,c} $a = 6.537$ Å $c = 5.316$ Å^{**,c}	$a = 6.535$ Å $c = 5.319$ Å con = 26.2%	$a = 6.446$ Å $c = 5.336$ Å con = 6.8%	$a = 6.541$ Å $a = 5.338$ Å con = 1.8%	–
Fe(Sn) ($A2$)	–	$a = 2.922$ Å con = 25.5%	$a = 2.928$ Å con = 22.2%	–	–
f_1 ($B2$)	–	–	$a = 2.996$ Å con = 20.9%	$a = 2.996$ Å con = 7.1%	–
f_2 ($D0_3/L2_1$)	–	–	$a = 6.017$ Å con = 16.4%	$a = 6.018$ Å con = 61.5%	$a = 6.023$ Å con = 14.3%
f_3 ($D0_3/L2_1$)	–	–	$a = 6.046$ Å con = 10.3%	$a = 6.046$ Å con = 13.1%	$a = 6.047$ Å con = 54.6%
f_4 ($D0_3/L2_1$)	$a = 6.06964$ Å^{d}	–	$a = 6.073$ Å con = 4.3%	$a = 6.071$ Å con = 5.3%	$a = 6.068$ Å con = 28.2%
Sn ($A5$)	–	$a = 5.836$ Å $c = 3.182$ Å con = 11.0%	$a = 5.836$ Å $c = 3.181$ Å con = 4.0%	$a = 5.837$ Å $c = 3.182$ Å con = 3.3%	$a = 5.838$ Å $a = 3.181$ Å con = 2.9%

^{a}[5], ^{b}[12], ^{c}[13], ^{d}[6], *powder sample, **single crystal

of structure occur and the contribution of them increase very fast with titanium concentration. These contributions were analyzed as the superposition of four different components: one with $B2$ (denoted as f_1) and three with $D0_3/L2_1$ types of structure (denoted as f_2, f_3, and f_4, respectively). It is shown in Fig. 3.

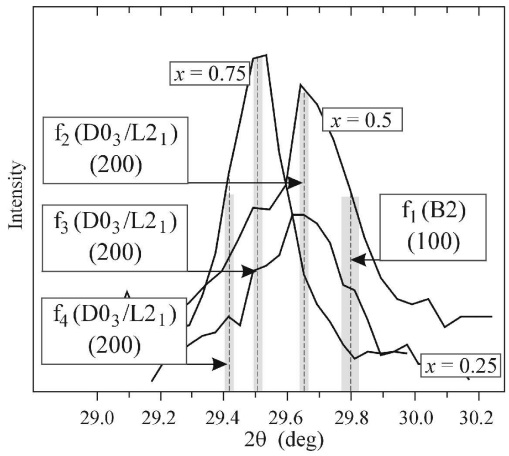


Fig. 3. Discrete components of X-ray patterns.

The lattice parameters of these contributions (f) are almost independent of Ti atoms concentration, however their contributions change considerably (Table). The phase with $B2$ structure exists in $Fe_{3-x}Ti_xSn$ system only when $x = 0.25$ and 0.5. On the basis of data from [14] it is very probable that content of Sn atoms is close to a value of about 50 at.%.

The phases denoted as f_2, f_3 and f_4 exist in the range of titanium concentration parameter from $x = 0.25$ to $x = 0.75$. The analysis of the relative intensities of the (111), (200) and (220) peaks shows that Sn atoms occupies mainly 4a site, Fe atoms occupy 8c site and partially 4b site and Ti atoms occupy 4b site. On the basis of this analysis the stoichiometry of f_2, f_3 and f_4 contribution could be estimated as to be close to $Fe_{2.5}Ti_{0.5}Sn$, $Fe_{2.25}Ti_{0.75}Sn$ and Fe_2TiSn, respectively. The contribution of Fe_2TiSn phase (f_4) increases from 4.3% (for $x = 0.25$) to 28.2% (for $x = 0.75$). The lattice parameter of this phase is similar to this for ideal Fe_2TiSn Heusler structure reported in paper [7].

The X-ray diffraction patterns of studied $Fe_{3-x}Ti_xSn$ disordered alloys exhibited an impurity of 3–11% of metallic Sn.

The obtained Mössbauer spectra of $Fe_{3-x}Ti_xSn$ disordered alloys are collected in Fig. 4. In the first step they were fitted by means of hyperfine field distribution method [11]. The results are shown in Fig. 5.

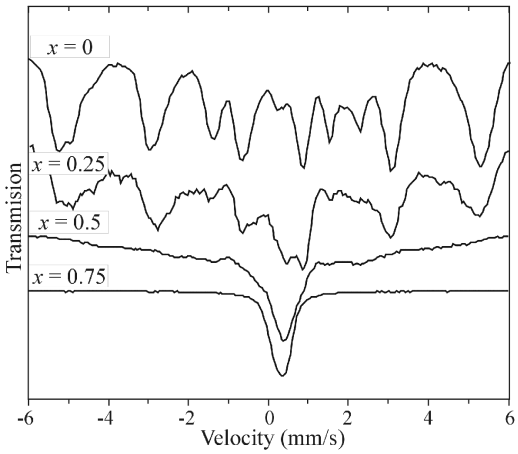


Fig. 4. Mössbauer spectra of the $Fe_{3-x}Ti_xSn$ disordered alloys.

The dominating high-magnetic phase in $Fe_{3-x}Ti_xSn$ disordered alloys with $x = 0$ and $x = 0.25$ is associated with Fe(Sn) alloy and additionally (for $x = 0.25$) with magnetic surroundings of Fe atoms existing in FeSn phase with $B2$ type of structure. Contribution to the distributions of hyperfine magnetic field in the range of B_{hf} from 100 kG to 300 kG comes mainly from FeSn ($B2$) and also from ternary Fe–Ti–Sn ($D0_3/L2_1$) alloys. The FeSn ($B35$) and $FeSn_2$ ($C16$) phases are seen close to the value of 100 kG. And finally, the contributions with low value of

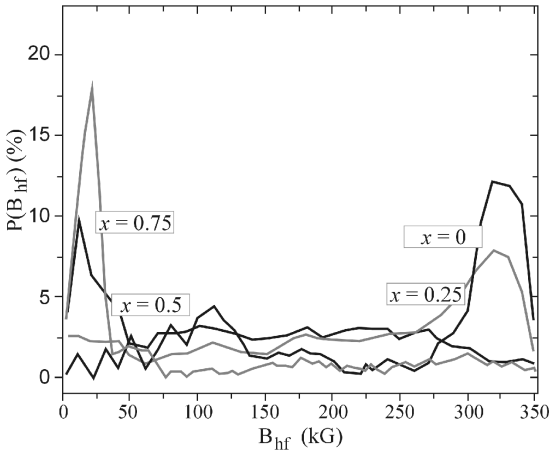


Fig. 5. Distributions of hyperfine magnetic fields obtained from fitting of the spectra.

hyperfine magnetic field ($B_{\rm hf} < 100$ kG) are associated with Fe–Ti–Sn ($D0_3/L2_1$) alloys again.

During the further analysis, the Mössbauer spectra were fitted with the discrete number of components (i.e. a single line, quadruple doublet or the Zeeman sextet). The X-ray study results together with the results of computer simulations of the Mössbauer spectra shapes for different types of the atomic ordering and different values of hyperfine parameters were taken into account during this analysis. However only nearest neighborhood of iron atoms were considered during these simulations.

It is known from literature that both FeSn ($B35$) and $FeSn_2$ ($C16$) phases have very similar set of hyperfine parameter values at room temperature. In the first of them the value of $B_{\rm hf} = 100 \div 110$ kG and IS parameter varies from 0.35 mm/s to 0.41 mm/s [15, 16]. The $FeSn_2$ phase has the following hyperfine parameters: $B_{\rm hf} = 113$ kG and IS = 0.51 mm/s [12]. For some technical procedures these phases could be also non-magnetic at room temperature [15, 16]. For samples studied in this paper, both of them are magnetic and were fitted in the range of the x parameter from 0 to 0.5 by means of one sextet with the value of hyperfine magnetic field changing form 112 kG to 106 kG and the value of the isomer shift changing from 0.045 mm/s to 0.37 mm/s.

The phases with $A2$, $B2$, and $D0_3/L2_1$ type of structure were analyzed in such a way that each Mössbauer subspectrum describes nonequivalent Fe site with the same number of Fe atoms in the nearest neighborhood. The values of hyperfine magnetic field played a critical role.

In Figs. 6 and 7 there are shown, respectively, contributions of Fe sites with appropriate number of Fe atoms and values of hyperfine magnetic field ($B_{\rm hf}$) at the Fe sites as a function of the number of Fe atoms in the nearest neighborhood,

respectively. As it is seen, the influence of a single Fe atom on the value of B_{hf} parameter is almost independent of titanium concentration for high values and very sensitive on it for low values.

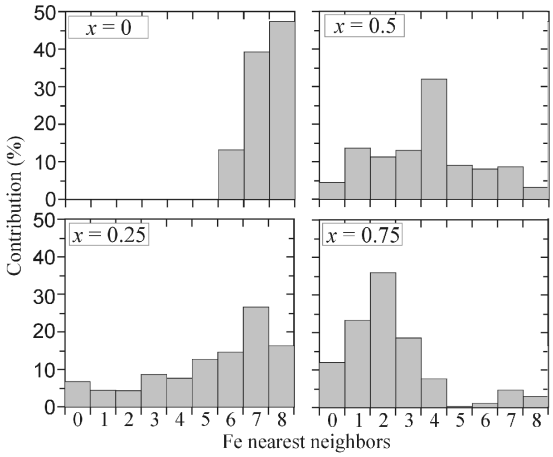


Fig. 6. Contributions of Fe sites with appropriate number of Fe atoms in the nearest neighborhood.

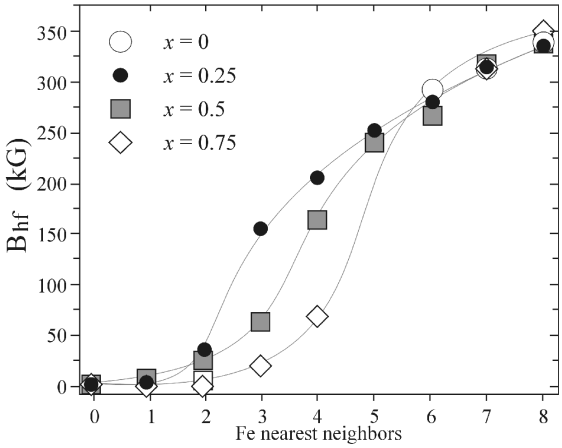


Fig. 7. Values of hyperfine magnetic field (B_{hf}) at the Fe sites as a function of the number of Fe atoms in the nearest neighborhood.

The analysis of the distributions shown in Fig. 6 confirms the results of X-ray studies that a mixture of phases with $B2$ and $D0_3/L2_1$ type consists of phases with an approximate stoichiometry of $Fe_{2.5}Ti_{0.5}Sn$, $Fe_{2.25}Ti_{0.75}$ and Fe_2TiSn. These results also confirm earlier conclusion that Sn atoms occupy manly 4a site, Fe atoms occupy 8c and partially 4b site and Ti atoms occupy 4b site.

Acknowledgments

The author would like to thank Dr M. Karolus from Institute of Materials Sciences for making the X-ray measurements.

References

[1] I. Vincze, A. Aldred, *Phys. Rev. B* **9**, 3845 (1974).

[2] V.A. Niculescu, T.J. Burch, J.I. Budnick, *J. Magn. Magn. Mater.* **39**, 223 (1983).

[3] Y. Nishino, M. Matsuo, S. Asano, *Phys. Rev. B* **44**, 12406 (1991).

[4] Y. Nishino, S. Inoue, S. Asano, *Phys. Rev. B* **48**, 13607 (1993).

[5] G. Trumpy, E. Both, C. Djega-Mariadassou, P. Lecocq, *Phys. Rev. B* **2**, 3477 (1970).

[6] A. Szytuła, Z. Tomkowicz, M. Turowski, *Acta Phys. Pol. A* **44**, 147 (1973).

[7] A. Jezierski, A. lebarski, *J. Magn. Magn. Mater.* **223**, 33 (2001).

[8] M. Nakabayashi, K. Fukuda, H. Kitagawa, Y. Yamada, S. Kubo, A. Matsushita, *Physica B* **329-333**, 1134 (2003).

[9] J.E. Frackowiak, K. Brzakalik, J. Deniszczyk, *J. Alloys Comp.* **442**, 242 (2007).

[10] W. Krans, G. Nolze, *J. Appl. Crystallogr.* **29**, 301 (1996).

[11] J. Hesse, A. Rübartsch, *J. Phys. E* **7**, 526 (1974).

[12] G. Le Caër, B. Malaman, G. Venturini, D. Fruchart, B. Roques, *J. Phys. F, Met. Phys.* **15**, 1813 (1985).

[13] G. Venturini, B. Malaman, G. Le Car, D. Fruchart, *Phys. Rev. B* **35**, 7038 (1987).

[14] E.P. Yelsukov, E.V. Voronina, G.N. Konygin, V.A. Barinov, S.K. Godovikov, G.A. Dorofeev, A.V. Zagainov, *J. Magn. Magn. Mater.* **166**, 334 (1997).

[15] L. Haggstrom, T. Ericsson, R. Wappling, K. Chandra, *Phys. Scr.* **11**, 47 (1975).

[16] Ou Mao, R.A. Dunlap, J.R. Dahn, *Solid State Ionics* **118**, 99 (1999).